

## PATENT ABSTRACTS OF JAPAN

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## (54) PAPER SURFACE IMPROVER

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a surface coating agent comprising an aqueous solution of a high-molecular but lowly viscous acrylamide polymer.

SOLUTION: This improver comprises an aqueous solution of an acrylamide polymer obtained by subjecting an aqueous solution of a mixture comprising at least 40 mol% acrylamide, 0.1-30 mol% anionic monomer, and 0.05-10 mol% methacrylonitrile to a polymerization reaction. It is desirable that the aqueous solution of the mixture further contains at least one member selected from among a vinyl cyanide compound, a crosslinking agent, and a chain transfer agent in an amount of 0.1-45 mol% based on the entire weight of the monomers constituting the acrylamide polymer when the mixture contains the vinyl cyanide compound, 0.005-3 mol% based on the entire weight of the monomers when it contains the crosslinking agent, or 0.01-8 mol% based on the entire weight of the monomers when it contains the chain transfer agent.

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CLAIMS

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[Claim(s)]

[Claim 1] The surface coating agent which consists of an acrylamide system polymer water solution obtained by giving the mixed water solution containing more than acrylamide 40 mol % and 0.1-30 mol % and 0.05-10 mol [ of methacrylonitriles ] % of anionic monomers to a polymerization reaction.

[Claim 2] For a mixed water solution, in the case of 0.1-45-mol % and a cross linking agent, a case is a 0.01-8-mol % and according to claim 1 surface [ which come to contain further ] coating agent to a total monomer total amount to a total monomer total amount to the total monomer total amount from which an acrylamide system polymer is constituted for at least one of a vinylcyanide compound, a cross linking agent, and the chain transfer agents in the case of a vinylcyanide compound to 0.005-3-mol % and a chain transfer agent.

[Claim 3] The surface coating agent according to claim 1 or 2 whose polymerization reaction is what completes a polymerization further after making a prepolymer form in the first step.

[Claim 4] The surface coating agent according to claim 1 to 3 which comes to add ureas to a product after giving a polymerization reaction.

[Claim 5] The surface coating agent according to claim 1 to 4 which uses persulfate as a polymerization catalyst.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the surface coating agent which can demonstrate the outstanding effectiveness, such as surface reinforcement, internal reinforcement, and waterproof improvement, by carrying out coating to a paper front face.

[0002]

[Description of the Prior Art] In recent years, in the paper manufacture industry, use of used paper and a broad-leaved tree progresses, and it is in the inclination which the content of a microfilament increases also in a print sheet, therefore association between fiber becomes weaker, and the reinforcement of paper has become is hard to be obtained. On the other hand, improvement in the speed and quality improvement progress, and presswork has come to require properties, such as higher surface reinforcement of level, internal reinforcement, and a water resisting property, from a print sheet. Since it corresponded to these demands, outside \*\* (coating) was carried out [ internal and ] more often in drugs. Although the yield of drugs will become low and it will especially become easy to generate the trouble on operation of machine dirt etc. if there is much amount used in the case of internal drugs, in outside \*\*\*\*\*, it becomes advantageous also from the yield being about 100% on operation.

[0003] There are things, such as cellulose systems, such as starch systems, such as oxidization starch, and a carboxymethyl cellulose, a polyvinyl alcohol (it omits Following PVA) system, and an acrylamide system polymer, as a surface coating agent by which coating is conventionally carried out in order to raise the surface reinforcement of paper, and a printability. On the occasion of use, a cooking process is required for the drugs of the starch system currently used or a PVA system, and they have various problems, such as foaming at the time of coating, and machine dirt, the top where workability is bad. [ most ] Furthermore, in the case of the drugs of a starch system, there are also problems, such as putrefaction and aging.

[0004] on the other hand, as an acrylamide system polymer, the acrylamide system polymer which introduced the anion radical is proposed in order to improve surface reinforcement -- \*\*\*\* (JP,43-27529,B) -- the improvement effect of surface reinforcement was not enough.

[0005] in order to improve these, use of the acrylamide system polymer containing a vinyl compound, a specific cross-linking monomer, and specific partial saturation dicarboxylic acid is proposed -- \*\*\*\* (JP,9-169946,A) -- the case where these cross linking agents are used -- a product -- hypoviscosity-izing -- or it is easy to do hyperviscosity and gelation of, and viscosity control is difficult. moreover, the bottom of existence of ureas -- an acrylamide system polymer -- a polymerization -- carrying out -- a front face -- quality of paper -- obtaining an improver is proposed -- \*\*\*\* (JP,5-302298,A, 8-260384) -- a urea decomposes by high pH-ization at the time of the temperature up in the case of a polymerization, and hydrolysis, the foaming phenomenon of a \*\* tone polymer occurs, and it becomes a manufacture top problem.

[0006]

[Problem(s) to be Solved by the Invention] This invention is faced obtaining the acrylamide system polymer of the letter of branching which is hypoviscosity, having the same amount of macromolecules as the conventional technique, a polymerization is controlled more to stability,

branching structure is introduced into homogeneity, and the surface coating agent which makes an active principle the polymer obtained in this way, and demonstrates the improvement effect of the outstanding surface reinforcement is offered.

[0007]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for attaining the purpose by using the acrylamide system copolymer obtained by copolymerizing the monomer mixture which contains the methacrylonitrile which shows the chain transfer effectiveness and the bridge formation effectiveness as an indispensable component, as a result of repeating research wholeheartedly, in order to develop surface coating \*\*\*\* which has the further high engine performance. That is, this invention is a surface coating agent which consists of an acrylamide system polymer water solution obtained by giving the mixed water solution containing more than acrylamide 40 mol % and 0.1-30 mol % and 0.05-10 mol % of methacrylonitriles ] % of anionic monomers to a polymerization reaction.

[0008] In this invention, as acrylamides, acrylamide and/or methacrylamide are used, and these may be used independently and may use both together.

[0009] As an example of an anionic monomer, the organic acid of the sulfonic-acid system which has vinyl groups, such as dicarboxylic acid systems, such as monocarboxylic acid systems, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a maleic acid, a fumaric acid, an itaconic acid, and a citraconic acid, a vinyl sulfonic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, is mentioned. Salts, such as the sodium salt and potassium salt, are sufficient as these organic acids. Moreover, these anionic monomers may be used independently and may use two or more kinds.

[0010] acrylamide and/or methacrylamide -- more than 40 mol % -- desirable -- more than 60 mol % and an anionic monomer -- 0.1-30-mol % -- desirable -- 0.5-20-mol % and a methacrylonitrile -- 0.05-10-mol % -- desirable -- 0.1-5-mol % -- it comes out comparatively.

[0011] A mixed water solution may be made to contain at least one of a vinylcyanide compound, a cross linking agent, and the chain transfer agents further in this invention. As a vinylcyanide compound, it is mentioned with ethylene system nitril compounds, such as a methacrylonitrile and acrylonitrile which has similar structure. all the monomers from which the amount of these vinylcyanide compound constitutes an acrylamide system polymer -- receiving -- 0.1-45-mol % -- it is 0.1-35-mol % preferably.

[0012] moreover, as an example of a cross linking agent Methylenebis Acrylamide, an ethylene screw (Meta) 2 functionality cross linking agents, such as acrylamide, ethylene GURIKORUJI (meta) acrylamide, diethylene GURIKORUJI (meta) acrylamide, TORIECHIRENGURIKORUJI (meta) acrylamide, a divinylbenzene, and diaryl acrylamide, (Meta) Or polyfunctional cross linking agents, such as 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, thoria krill acid pentaerythritol, trimethylol propane acrylate, and diacryloyl imide, N-permutation acrylamide system monomers, such as dimethyl acrylamide, diacetone acrylamide, and isopropyl acrylamide, are mentioned. In addition, a cross linking agent is the range which does not spoil the purpose of stabilization of polymerization control of this invention, and can be used together if needed.

[0013] although these cross linking agents can use together one sort or two sorts or more, in order [ as mentioned above, ] to also commit the bridge formation effectiveness by the methacrylonitrile itself -- a cross-linking condition usual in the amount used -- being little -- the total amount of all monomers -- receiving -- 0.005-3-mol % -- it is 0.01-1-mol % preferably.

[0014] Moreover, a chain transfer agent can be used in the range which does not spoil the purpose of stabilization of polymerization control of this invention. As an example of a chain transfer agent, the thing of allyl compound systems, such as mercapto systems, such as mercaptoethanol besides isopropyl alcohol, thiourea, thioglycolic acid, mercaptopropionic acid, thiosalicylic acid, thiolactic acid, an aminoethane thiol, thioglycerol, and thiomalic acid, allyl alcohol, allyl compound sulfonic-acid soda, and meta-allyl compound sulfonic-acid soda, is mentioned.

[0015] although these chain transfer agents can use one sort or two sorts or more, in order for the methacrylonitrile itself which is an indispensable component to do the chain transfer

effectiveness so -- a case usual in the amount used -- being little -- the total amount of all monomers -- receiving -- 0.01-8-mol % -- it is 0.03-4-mol % preferably.

[0016] It is the range which does not spoil the purpose of the improvement in surface on the strength of this invention other than the component described above as a monomer, and other monomer components can also be made to contain in this invention. A cationic monomer and the Nonion nature monomer are mentioned as such a monomer component.

[0017] Acrylamide (meta) derivatives, such as acrylic ester (meta) derivative [, such as dialkyl aminoethyl (meta) acrylate which is the monomer which has the third class amino group as a cationic monomer, and dialkyl aminopropyl (meta) acrylate, ], dialkyl aminoethyl (meta) acrylamide, dialkyl aminopropyl (meta) acrylamide, and acrylamide (meta)-3-methylbutyl dimethylamine, can be mentioned. In addition, as a cationic monomer, the salt of the monomer which has the above-mentioned third class amino group can be used. As a salt, a salt with an inorganic acid like a hydrochloric acid and a sulfuric acid is sufficient, and a salt with an organic acid like a formic acid and an acetic acid is sufficient. Furthermore, the quaternary salt which formed the third class amino group into 4 class by methyl chloride, methyl bromide, benzyl chloride, benzyl bromide, the dimethyl sulfate, epichlorohydrin, etc. is sufficient. Moreover, a cationic monomer may be used independently and may use two or more kinds.

[0018] Furthermore, as an Nonion nature monomer, diacetone acrylamide, alkyl acrylate, hydroxy acrylate, vinyl acetate, styrene, alpha methyl styrene, etc. are mentioned.

[0019] Moreover, a urea is desirable, although ureas may be added after a polymerization reaction in this invention and a urea, thiourea, an ethylene urea, etc. are mentioned as such ureas. the weight ratio of a urea/monomers -- 2 - 50%/-- they are 10 - 40% / 90 - 60% preferably 98 to 50%. The system of reaction is possible for addition of ureas, if temperature falls to at least 90 degrees C or less by cooling, a polymerization is completed and it is 85-60 degrees C preferably. In addition, in JP,5-302298,A, although performing a polymerization reaction under existence of a urea is shown, by this approach, by heat or pH change, a urea decomposes, it foams, and there is a problem of the ability of workability not to make the whole quantity of the prepared urea exist in a product by the bad loss of the urea under reaction. In this invention, actuation becomes easy, without the loss and foaming phenomenon by decomposition of a urea at the time of a polymerization arising by adding a urea after a polymerization.

[0020] In this invention, it faces giving a mixed water solution to a polymerization reaction, and various well-known polymerization methods can apply conventionally. For example, in addition to this, a monomer, a cross linking agent, and a chain transfer agent can be taught to a predetermined reaction container said indispensable monomer and water, and if needed, a catalyst can be added, and the target acrylamide system polymer water solution (a copolymer water solution may be called hereafter) can be obtained by warming under stirring. Moreover, while a part or all of a monomer is dropped into a reaction container, you may make it react. After a catalyst injection makes a prepolymer form by the 1st step of reaction, you may make it obtain the copolymer water solution containing the polymer of the high amount of macromolecules of whenever [ branching ] by adding a catalyst and completing a polymerization further, although at least 1 time is possible. Reaction temperature is about 40-100 degrees C, and reaction time is usually about 0.5 - 8 hours.

[0021] If a catalyst is a radical polymerization initiator usually used for the polymerization reaction in a water solution as a polymerization initiator, it will not be restricted especially and a bromate catalyst like a persulfate catalyst like a hydrogen peroxide, a benzoyl peroxide, a peroxide catalyzer like t-butyl peroxide, ammonium persulfate, sodium persulfate, and potassium persulfate, sodium bromate, and a potassium bromate and a fault boron acid chloride catalyst like fault boron acid sodium will be mentioned. Moreover, the redox system catalyst and azo system catalyst which combined with these the sulfite and hydrogensulfite which are a reducing agent, the transition-metals salt, the organic amine, etc. can also be used. These may be used independently and may be used combining two or more kinds. the amount of these catalysts used -- the AUW of a monomer -- receiving -- 0.01 - 10wt% -- it is 0.05 - 4wt% preferably.

[0022] Although the above-mentioned catalyst is usable as an additional catalyst, catalyst

effectiveness and a cost side to persulfate is the most suitable. Of course, after prepolymer generation does not need to add a catalyst, especially when a catalyst remains so much. It is 40 degrees C or more, and the temperature of an additional polymerization reaction is 70-95 degrees C preferably, and is good to consider as an elevated temperature rather than the 1st step of reaction temperature. the amount used -- 0.01 - 10wt% -- it is 0.05 - 4wt% preferably. A monomer can also be added if needed in the case of this catalyst addition. The monomer presentation in this case may be the same as an initial preparation monomer presentation at the 1st step of reaction, or may differ.

[0023] In this invention, while resonance stabilization of the radical generated according to the radical catalyst by using a methacrylonitrile as an indispensable component is carried out by the nitrile group of a methacrylonitrile and it carries out chain transfer agent-work, the point by the abstraction reaction from a methyl group constructing a bridge is formed. Thus, by the methacrylonitrile independent, a cross linking agent/chain transfer agent works, it makes, there is also no rapid viscosity rise by this, and control of a polymerization reaction becomes easy.

[0024] the copolymer water solution in which according to this invention approach hypoviscosity is shown though it is the amount of macromolecules -- easy -- it can obtain -- this copolymer water solution -- a front face -- quality of paper -- not only the surface reinforcement of paper but an improvement effect high also in respect of internal division reinforcement is acquired by using it as an improver. The surface coating agent of this invention can be used combining various drugs, such as a surface sizing compound besides surface coating agents, such as a starch system, a PVA system, a cellulose system, and a polyacrylamide system, a deck-watertight-luminaire-ized agent, a non-skid agent, antiseptics, a defoaming agent, a release agent, and a color.

[0025] In using the surface coating agent of this invention, it is desirable when considering as the coating liquid concentration of 0.1 - 10% and the viscosity of 3-350cps carries out coating. As the coating approach, the approach currently generally performed, size press, a gate roll coater, a calender, a blade coating machine, a spray, etc. are mentioned. Moreover, the coating agent of this invention can be applied to various stencil paper, such as the paper boards, such as a liner and a coat ball, coat stencil paper (acidity, neutrality), a PPC form, a form form, a print sheet, a newsprint, and inkjet printing paper, and is very effective also in improvement in the internal reinforcement of not only improving the reinforcement of fuzz, a bessel pick, paper powder, and another surface wear nature and papers front face but paper.

[0026]

[Embodiment of the Invention] An example and the example of a comparison are given to below, and this invention is more concretely explained to it. In addition, each of sections and %s is weight criteria as long as there is no special mention.

[0027] The 50% acrylamide water-solution 338 section, the acrylic-acid 20 section, the methacrylonitrile 9.4 section, and the water 500 section were taught to the 4 opening flask equipped with example 1 agitator, a thermometer, a ring current cooling pipe, and nitrogen gas installation tubing, acidity or alkalinity was adjusted to pH3.5 with alkali, and the oxygen in the system of reaction was removed through nitrogen gas. The inside of a system was made into 40 degrees C, and the ammonium persulfate water-solution 40 section and the 10% sodium-hydrogensulfite water-solution 24 section were supplied 10% as a polymerization initiator to the bottom of stirring. After the system of reaction carried out the temperature up to 90 degrees C, the ammonium persulfate water-solution 20 section was added 10 more%, and this temperature was held for 2 hours. The water 50 section was supplied after polymerization termination, and the copolymer water solution of pH4.7, the solid content of 20.4%, the viscosity (25 degrees C) of 8400cps, and weight average molecular weight 1,650,000 was obtained.

[0028] In two to example 10 example 1, the class or its operating rate of a copolymerization component was changed as shown in Table 1 and 2, the same actuation as an example 1 was performed [ the amount of catalysts was adjusted so that it might become suitable viscosity, and also ], and various copolymer water solutions were obtained. After cooling to 85 degrees C - about 80 degrees C after polymerization termination, the urea addition article after an example 6 added and obtained the urea so that it might grow into Table 2 with the urea content of the

specified quantity of a publication to the total monomer weight. Examples 7 and 8 trickled separately a monomer / cross linking agent mixed liquor, and a catalyst / chain transfer agent mixed water solution into 80-degree C warm water over 120 minutes, performed the polymerization, and reacted by adding a catalyst like an example 1 after that. the description of the obtained various copolymer water solutions --- Table 3 is shown for a value.

[0029]

[Table 1]

	モノマーの種類と使用割合 (モル%)				
	AM	MAN	アニオン性 モノマー	AN	その他 モノマー
実施例 1	87	3	AA 10		
実施例 2	79	1	AA 5	15	
実施例 3	78.5	0.5	IA 6	15	
実施例 4	90	2	FA 3	5	
実施例 5	87.5	1.5	MA/IA 2/4	5	
実施例 6	76.8	0.2	AA 8	15	
実施例 7	72.2	0.8	IA/AA 2/5	20	
実施例 8	80.5	0.5	NSS 9	10	
実施例 9	87	1	AA/FA 5/5	10	DM 2
実施例 10	71	1	AA/NSS 10/3	15	
実施例 11	74.3	0.7	AA/IA 5/8	10	St 2
比較例 1	94		AA 6		
比較例 2	85		IA 5	10	
比較例 3	86		AA/NSS 5/4	5	
比較例 4	78		AA/IA 5/7	10	
比較例 5	74		AA/IA 8/3	15	

[0030]

[Table 2]

	架橋剤 (モル%)	連鎖移動剤 (モル%)	モノマー/尿素 (wt%)
実施例 1			
実施例 2		IPA 3	
実施例 3		MAS 0.1	
実施例 4	MBAM 0.02		
実施例 5	DMAM 0.5	AS 0.8	
実施例 6			10
実施例 7		IPA 1	15
実施例 8	MBAM 0.03	MAS 0.2	15
実施例 9			20
実施例 10	DMAM 0.8	AS 1	10
実施例 11	MBAM 0.02	IPA 2	10
比較例 1		IPA 5	
比較例 2		AS 0.8	
比較例 3	MBAM 0.03	MAS 0.3	
比較例 4	DMAM 0.8	MAS 0.4	
比較例 5	DMAM 1	MAS 0.3	15

[0031] the inside of Table 1 and 2, and AM:acrylamide and a MAN:methacrylonitrile anionic monomer --- carrying out --- as AA:acrylic acid, IA:itaconic acid, FA:fumaric acid, NSS:sodium styrenesulfonate, and a cross linking agent --- as MBAM:methylenebis acrylamide, DMAM:dimethyl acrylamide, and a chain transfer agent --- IPA: --- DM:dimethylaminoethyl

methacrylate and St:styrene are shown, respectively as isopropyl alcohol, MAS:meta-allyl compound sulfonic-acid soda, AS:allyl compound sulfonic-acid soda, and other monomers. [0032] In one to example of comparison 5 example 1, the class or its operating rate of a copolymerization component was changed as shown in Table 1 and 2, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. In the examples 3-5 of a comparison, although product viscosity tended to obtain the thing 5000cps or more, since it lifting-came to be easy of rapid thickening and gelation in the second half of a polymerization reaction, viscosity control was performed in the chain transfer agent, the amount of catalysts, etc., and the product of hypoviscosity was obtained. the description of the obtained various copolymer water solutions -- Table 3 is shown for a value.

[0033]

[Table 3]

	固形分 (%)	pH	粘度 (cps)	Mw (万)
実施例 1	20.4	4.7	8400	165
実施例 2	20.6	4.9	7200	143
実施例 3	20.7	5.2	6100	135
実施例 4	20.3	5.1	5200	172
実施例 5	20.4	4.9	6300	197
実施例 6	20.1	5.2	4800	138
実施例 7	20.2	5.3	4400	126
実施例 8	20.4	5.1	5100	221
実施例 9	20.5	5.3	3700	126
実施例 10	20.1	5.2	5600	173
実施例 11	20.3	5.2	4900	152
比較例 1	20.4	4.8	9700	48
比較例 2	20.6	4.9	7600	43
比較例 3	20.7	5.1	2800	145
比較例 4	20.5	5.0	3900	161
比較例 5	20.3	5.3	1800	168

[0034]

[The coating approach] The basis weight of 43g/m<sup>2</sup> Newspaper stencil paper was cut out to 12cm long and 24cm wide, and the upper part of paper was fixed with the Scotch tape on the flat glass plate. The compound polymer was diluted with water to 3% and 2%, and coating was carried out to one side using the coating roll bar of No.3. the place which measured the liquid adsorption of coating liquid -- 8.2 g/m<sup>2</sup> it is -- 3% diluent -- 0.25 g/m<sup>2</sup> and 2% diluent -- 0.16 g/m<sup>2</sup> It was the amount of coating. It dried for 90 seconds with the drum dryer immediately adjusted to 105 degrees C after coating, and sample paper was obtained. Evaluation was carried out for the obtained sample paper after gas conditioning one whole day and night by the air conditioned room (temperature of 20 degrees C, 65% of humidity).

[0035]

[The evaluation approach] Measurement was performed according to the approach shown below.

- RI pick : the display which observed a RI-II mold printing testing machine (product made from \*\*\*\*\*), Toyo Ink, the ink tuck 15, the amount of ink of 2ml, rotational frequency 60rpm, and the \*\*\*\*\* condition after printing with the naked eye, made 5 good, and made 1 \*\* estimated. The numeric value was expressed as the average of printing evaluation of five sheets.
- Internal reinforcement : internal bond tester (Kumagaya Riki Kogyo K.K. make)
- Breaking length : JIS P 8113 [0036]

[Table 4]



	R I ピック		インターナル・ブンド		裂断長	
	(a)	(b)	(a)	(b)	(a)	(b)
実施例 1	3.7	4.6	1.41	1.50	2.80	2.90
実施例 2	4.0	4.5	1.40	1.48	2.79	2.88
実施例 3	3.9	4.6	1.39	1.48	2.82	2.93
実施例 4	4.1	4.7	1.42	1.52	2.83	2.96
実施例 5	4.3	4.8	1.44	1.56	2.81	2.93
実施例 6	4.2	4.9	1.45	1.54	2.80	2.94
実施例 7	4.1	4.8	1.43	1.53	2.82	2.93
実施例 8	4.2	4.6	1.41	1.50	2.79	2.91
実施例 9	3.9	4.4	1.40	1.51	2.76	2.87
実施例 10	4.0	4.5	1.42	1.53	2.81	2.89
実施例 11	4.1	4.6	1.44	1.54	2.78	2.86
比較例 1	3.1	4.0	1.37	1.44	2.72	2.84
比較例 2	3.3	4.1	1.36	1.45	2.71	20.82
比較例 3	3.5	4.2	1.34	1.42	2.73	2.80
比較例 4	3.4	4.2	1.35	1.43	2.74	2.83
比較例 5	3.6	4.3	1.36	1.46	2.76	2.84

(a) : 塗工量 - 0.16 g/m<sup>2</sup>(b) : 塗工量 - 0.25 g/m<sup>2</sup>

[0037]

[Effect of the Invention] as shown in Table 3, while according to this invention it is possible to control the viscosity of a copolymer water solution in the large range and problems, such as gelation, stop being able to happen easily, it is shown in Table 4 -- as -- a front face -- quality of paper -- the outstanding effectiveness of raising surface reinforcement as an improver is demonstrated.

[Translation done.]

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the surface coating agent which can demonstrate the outstanding effectiveness, such as surface reinforcement, internal reinforcement, and waterproof improvement, by carrying out coating to a paper front face.

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PRIOR ART

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[Description of the Prior Art] In recent years, in the paper manufacture industry, use of used paper and a broad-leaved tree progresses, and it is in the inclination which the content of a microfilament increases also in a print sheet, therefore association between fiber becomes weaker, and the reinforcement of paper has become is hard to be obtained. On the other hand, improvement in the speed and quality improvement progress, and presswork has come to require properties, such as higher surface reinforcement of level, internal reinforcement, and a water resisting property, from a print sheet. Since it corresponded to these demands, outside \*\* (coating) was carried out [ internal and ] more often in drugs. Although the yield of drugs will become low and it will especially become easy to generate the trouble on operation of machine dirt etc. if there is much amount used in the case of internal drugs, in outside \*\*\*\*\*, it becomes advantageous also from the yield being about 100% on operation.

[0003] There are things, such as cellulose systems, such as starch systems, such as oxidization starch, and a carboxymethyl cellulose, a polyvinyl alcohol (it omits Following PVA) system, and an acrylamide system polymer, as a surface coating agent by which coating is conventionally carried out in order to raise the surface reinforcement of paper, and a printability. On the occasion of use, a cooking process is required for the drugs of the starch system currently used or a PVA system, and they have various problems, such as foaming at the time of coating, and machine dirt, the top where workability is bad. [ most ] Furthermore, in the case of the drugs of a starch system, there are also problems, such as putrefaction and aging.

[0004] on the other hand, as an acrylamide system polymer, the acrylamide system polymer which introduced the anion radical is proposed in order to improve surface reinforcement -- \*\*\*\* (JP,43-27529,B) -- the improvement effect of surface reinforcement was not enough.

[0005] in order to improve these, use of the acrylamide system polymer containing a vinyl compound, a specific cross-linking monomer, and specific partial saturation dicarboxylic acid is proposed -- \*\*\*\* (JP,9-169946,A) -- the case where these cross linking agents are used -- a product -- hypoviscosity-izing -- or it is easy to do hyperviscosity and gelation of, and viscosity control is difficult. moreover, the bottom of existence of ureas -- an acrylamide system polymer -- a polymerization -- carrying out -- a front face -- quality of paper -- obtaining an improver is proposed -- \*\*\*\* (JP,5-302298,A, 8-260384) -- a urea decomposes by high pH-ization at the time of the temperature up in the case of a polymerization, and hydrolysis, the foaming phenomenon of a \*\* tone polymer occurs, and it becomes a manufacture top problem.

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[Translation done.]

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EFFECT OF THE INVENTION

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[Effect of the Invention] as shown in Table 3, while according to this invention it is possible to control the viscosity of a copolymer water solution in the large range and problems, such as gelation, stop being able to happen easily, it is shown in Table 4 -- as -- a front face -- quality of paper -- the outstanding effectiveness of raising surface reinforcement as an improver is demonstrated.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention is faced obtaining the acrylamide system polymer of the letter of branching which is hypoviscosity, having the same amount of macromolecules as the conventional technique, a polymerization is controlled more to stability, branching structure is introduced into homogeneity, and the surface coating agent which makes an active principle the polymer obtained in this way, and demonstrates the improvement effect of the outstanding surface reinforcement is offered.

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MEANS

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[Means for Solving the Problem] this invention persons came to complete a header and this invention for attaining the purpose by using the acrylamide system copolymer obtained by copolymerizing the monomer mixture which contains the methacrylonitrile which shows the chain transfer effectiveness and the bridge formation effectiveness as an indispensable component, as a result of repeating research wholeheartedly, in order to develop surface coating \*\*\*\* which has the further high engine performance. That is, this invention is a surface coating agent which consists of an acrylamide system polymer water solution obtained by giving the mixed water solution containing more than acrylamide 40 mol % and 0.1-30 mol % and 0.05-10 mol [ of methacrylonitriles ] % of anionic monomers to a polymerization reaction.

[0008] In this invention, as acrylamides, acrylamide and/or methacrylamide are used, and these may be used independently and may use both together.

[0009] As an example of an anionic monomer, the organic acid of the sulfonic-acid system which has vinyl groups, such as dicarboxylic acid systems, such as monocarboxylic acid systems, such as an acrylic acid, a methacrylic acid, and a crotonic acid, a maleic acid, a fumaric acid, an itaconic acid, and a citraconic acid, a vinyl sulfonic acid, a styrene sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, is mentioned. Salts, such as the sodium salt and potassium salt, are sufficient as these organic acids. Moreover, these anionic monomers may be used independently and may use two or more kinds.

[0010] acrylamide and/or methacrylamide -- more than 40 mol % -- desirable -- more than 60 mol % and an anionic monomer -- 0.1-30-mol % -- desirable -- 0.5-20-mol % and a methacrylonitrile -- 0.05-10-mol % -- desirable -- 0.1-5-mol % -- it comes out comparatively.

[0011] A mixed water solution may be made to contain at least one of a vinylcyanide compound, a cross linking agent, and the chain transfer agents further in this invention. As a vinylcyanide compound, it is mentioned with ethylene system nitril compounds, such as a methacrylonitrile and acrylonitrile which has similar structure. all the monomers from which the amount of these vinylcyanide compound constitutes an acrylamide system polymer -- receiving -- 0.1-45-mol % -- it is 0.1-35-mol % preferably.

[0012] moreover, as an example of a cross linking agent Methylenebis Acrylamide, an ethylene screw (Meta) 2 functionality cross linking agents, such as acrylamide, ethylene GURIKORUJI (meta) acrylamide, diethylene GURIKORUJI (meta) acrylamide, TORIECHIRENGURIKORUJI (meta) acrylamide, a divinylbenzene, and diaryl acrylamide, (Meta) Or polyfunctional cross linking agents, such as 1, 3, 5-thoria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, thoria krill acid pentaerythritol, trimethylol propane acrylate, and diacryloyl imide, N-permutation acrylamide system monomers, such as dimethyl acrylamide, diacetone acrylamide, and isopropyl acrylamide, are mentioned. In addition, a cross linking agent is the range which does not spoil the purpose of stabilization of polymerization control of this invention, and can be used together if needed.

[0013] although these cross linking agents can use together one sort or two sorts or more, in order [ as mentioned above, ] to also commit the bridge formation effectiveness by the methacrylonitrile itself -- a cross-linking condition usual in the amount used -- being little -- the total amount of all monomers -- receiving -- 0.005-3-mol % -- it is 0.01-1-mol % preferably.

[0014] Moreover, a chain transfer agent can be used in the range which does not spoil the purpose of stabilization of polymerization control of this invention. As an example of a chain transfer agent, the thing of allyl compound systems, such as mercapto systems, such as mercaptoethanol besides isopropyl alcohol, thiourea, thioglycolic acid, mercaptopropionic acid, thiosalicylic acid, thiolactic acid, an aminoethane thiol, thioglycerol, and thiomalic acid, allyl alcohol, allyl compound sulfonic-acid soda, and meta-allyl compound sulfonic-acid soda, is mentioned.

[0015] although these chain transfer agents can use one sort or two sorts or more, in order for the methacrylonitrile itself which is an indispensable component to do the chain transfer effectiveness so -- a case usual in the amount used -- being little -- the total amount of all monomers -- receiving -- 0.01-8-mol % -- it is 0.03-4-mol % preferably.

[0016] It is the range which does not spoil the purpose of the improvement in surface on the strength of this invention other than the component described above as a monomer, and other monomer components can also be made to contain in this invention. A cationic monomer and the Nonion nature monomer are mentioned as such a monomer component.

[0017] Acrylamide (meta) derivatives, such as acrylic ester (meta) derivative [, such as dialkyl aminoethyl (meta) acrylate which is the monomer which has the third class amino group as a cationic monomer, and dialkyl aminopropyl (meta) acrylate, ], dialkyl aminoethyl (meta) acrylamide, dialkyl aminopropyl (meta) acrylamide, and acrylamide (meta)-3-methylbutyl dimethylamine, can be mentioned. In addition, as a cationic monomer, the salt of the monomer which has the above-mentioned third class amino group can be used. As a salt, a salt with an inorganic acid like a hydrochloric acid and a sulfuric acid is sufficient, and a salt with an organic acid like a formic acid and an acetic acid is sufficient. Furthermore, the quaternary salt which formed the third class amino group into 4 class by methyl chloride, methyl bromide, benzyl chloride, benzyl bromide, the dimethyl sulfate, epichlorohydrin, etc. is sufficient. Moreover, a cationic monomer may be used independently and may use two or more kinds.

[0018] Furthermore, as an Nonion nature monomer, diacetone acrylamide, alkyl acrylate, hydroxy acrylate, vinyl acetate, styrene, alpha methyl styrene, etc. are mentioned.

[0019] Moreover, a urea is desirable, although ureas may be added after a polymerization reaction in this invention and a urea, thiourea, an ethylene urea, etc. are mentioned as such ureas. the weight ratio of a urea/monomers -- 2 - 50%/-- they are 10 - 40% / 90 - 60% preferably 98 to 50%. The system of reaction is possible for addition of ureas, if temperature falls to at least 90 degrees C or less by cooling, a polymerization is completed and it is 85-60 degrees C preferably. In addition, in JP,5-302298,A, although performing a polymerization reaction under existence of a urea is shown, by this approach, by heat or pH change, a urea decomposes, it foams, and there is a problem of the ability of workability not to make the whole quantity of the prepared urea exist in a product by the bad loss of the urea under reaction. In this invention, actuation becomes easy, without the loss and foaming phenomenon by decomposition of a urea at the time of a polymerization arising by adding a urea after a polymerization.

[0020] In this invention, it faces giving a mixed water solution to a polymerization reaction, and various well-known polymerization methods can apply conventionally. For example, in addition to this, a monomer, a cross linking agent, and a chain transfer agent can be taught to a predetermined reaction container said indispensable monomer and water, and if needed, a catalyst can be added, and the target acrylamide system polymer water solution (a copolymer water solution may be called hereafter) can be obtained by warming under stirring. Moreover, while a part or all of a monomer is dropped into a reaction container, you may make it react. After a catalyst injection makes a prepolymer form by the 1st step of reaction, you may make it obtain the copolymer water solution containing the polymer of the high amount of macromolecules of whenever [ branching ] by adding a catalyst and completing a polymerization further, although at least 1 time is possible. Reaction temperature is about 40-100 degrees C, and reaction time is usually about 0.5 - 8 hours.

[0021] If a catalyst is a radical polymerization initiator usually used for the polymerization reaction in a water solution as a polymerization initiator, it will not be restricted especially and a

bromate catalyst like a persulfate catalyst like a hydrogen peroxide, a benzoyl peroxide, a peroxide catalyzer like t-butyl peroxide, ammonium persulfate, sodium persulfate, and potassium persulfate, sodium bromate, and a potassium bromate and a fault boron acid chloride catalyst like fault boron acid sodium will be mentioned. Moreover, the redox system catalyst and azo system catalyst which combined with these the sulfite and hydrogensulfite which are a reducing agent, the transition-metals salt, the organic amine, etc. can also be used. These may be used independently and may be used combining two or more kinds. the amount of these catalysts used -- the AUW of a monomer -- receiving -- 0.01 - 10wt% -- it is 0.05 - 4wt% preferably.

[0022] Although the above-mentioned catalyst is usable as an additional catalyst, catalyst effectiveness and a cost side to persulfate is the most suitable. Of course, after prepolymer generation does not need to add a catalyst, especially when a catalyst remains so much. It is 40 degrees C or more, and the temperature of an additional polymerization reaction is 70-95 degrees C preferably, and is good to consider as an elevated temperature rather than the 1st step of reaction temperature. the amount used -- 0.01 - 10wt% -- it is 0.05 - 4wt% preferably. A monomer can also be added if needed in the case of this catalyst addition. The monomer presentation in this case may be the same as an initial preparation monomer presentation at the 1st step of reaction, or may differ.

[0023] In this invention, while resonance stabilization of the radical generated according to the radical catalyst by using a methacrylonitrile as an indispensable component is carried out by the nitrile group of a methacrylonitrile and it carries out chain transfer agent-work, the point by the abstraction reaction from a methyl group constructing a bridge is formed. Thus, by the methacrylonitrile independent, a cross linking agent/chain transfer agent works, it makes, there is also no rapid viscosity rise by this, and control of a polymerization reaction becomes easy.

[0024] the copolymer water solution in which according to this invention approach hypoviscosity is shown though it is the amount of macromolecules -- easy -- it can obtain -- this copolymer water solution -- a front face -- quality of paper -- not only the surface reinforcement of paper but an improvement effect high also in respect of internal division reinforcement is acquired by using it as an improver. The surface coating agent of this invention can be used combining various drugs, such as a surface sizing compound besides surface coating agents, such as a starch system, a PVA system, a cellulose system, and a polyacrylamide system, a deck-watertight-luminaire-ized agent, a non-skid agent, antiseptics, a defoaming agent, a release agent, and a color.

[0025] In using the surface coating agent of this invention, it is desirable when considering as the coating liquid concentration of 0.1 - 10% and the viscosity of 3-350cps carries out coating. As the coating approach, the approach currently generally performed, size press, a gate roll coater, a calender, a blade coating machine, a spray, etc. are mentioned. Moreover, the coating agent of this invention can be applied to various stencil paper, such as the paper boards, such as a liner and a coat ball, coat stencil paper (acidity, neutrality), a PPC form, a form form, a print sheet, a newsprint, and inkjet printing paper, and is very effective also in improvement in the internal reinforcement of not only improving the reinforcement of fuzz, a bessel pick, paper powder, and another surface wear nature and papers front face but paper.

[0026]

[Embodiment of the Invention] An example and the example of a comparison are given to below, and this invention is more concretely explained to it. In addition, each of sections and %s is weight criteria as long as there is no special mention.

[0027] The 50% acrylamide water-solution 338 section, the acrylic-acid 20 section, the methacrylonitrile 9.4 section, and the water 500 section were taught to the 4 opening flask equipped with example 1 agitator, a thermometer, a ring current cooling pipe, and nitrogen gas installation tubing, acidity or alkalinity was adjusted to pH3.5 with alkali, and the oxygen in the system of reaction was removed through nitrogen gas. The inside of a system was made into 40 degrees C, and the ammonium persulfate water-solution 40 section and the 10% sodium-hydrogensulfite water-solution 24 section were supplied 10% as a polymerization initiator to the bottom of stirring. After the system of reaction carried out the temperature up to 90 degrees C, the ammonium persulfate water-solution 20 section was added 10 more%, and this temperature



was held for 2 hours. The water 50 section was supplied after polymerization termination, and the copolymer water solution of pH4.7, the solid content of 20.4%, the viscosity (25 degrees C) of 8400cps, and weight average molecular weight 1,650,000 was obtained.

[0028] In two to example 10 example 1, the class or its operating rate of a copolymerization component was changed as shown in Table 1 and 2, the same actuation as an example 1 was performed [ the amount of catalysts was adjusted so that it might become suitable viscosity, and also ], and various copolymer water solutions were obtained. After cooling to 85 degrees C - about 80 degrees C after polymerization termination, the urea addition article after an example 6 added and obtained the urea so that it might grow into Table 2 with the urea content of the specified quantity of a publication to the total monomer weight. Examples 7 and 8 trickled separately a monomer / cross linking agent mixed liquor, and a catalyst / chain transfer agent mixed water solution into 80-degree C warm water over 120 minutes, performed the polymerization, and reacted by adding a catalyst like an example 1 after that. the description of the obtained various copolymer water solutions -- Table 3 is shown for a value.

[0029]

[Table 1]

	モノマーの種類と使用割合 (モル%)				
	AM	MAN	アニオン性 モノマー	AN	その他 モノマー
実施例 1	87	3	AA 10		
実施例 2	79	1	AA 5	15	
実施例 3	78.5	0.5	IA 6	15	
実施例 4	90	2	FA 3	5	
実施例 5	87.5	1.5	MA/IA 2/4	5	
実施例 6	76.8	0.2	AA 8	15	
実施例 7	72.2	0.8	IA/AA 2/5	20	
実施例 8	80.5	0.5	NSS 9	10	
実施例 9	87	1	AA/FA 5/5	10	DM 2
実施例 10	71	1	AA/NSS 10/3	15	
実施例 11	74.3	0.7	AA/IA 5/8	10	St 2
比較例 1	94		AA 6		
比較例 2	85		IA 5	10	
比較例 3	86		AA/NSS 5/4	5	
比較例 4	78		AA/IA 5/7	10	
比較例 5	74		AA/IA 8/3	15	

[0030]

[Table 2]

	架橋剤 (モル%)	連鎖移動剤 (モル%)	モ/マ-/尿素 (wt%)
実施例 1			
実施例 2		IPA 3	
実施例 3		MAS 0.1	
実施例 4	MBAM 0.02		
実施例 5	DMAM 0.5	AS 0.8	
実施例 6			10
実施例 7		IPA 1	15
実施例 8	MBAM 0.03	MAS 0.2	15
実施例 9			20
実施例 10	DMAM 0.8	AS 1	10
実施例 11	MBAM 0.02	IPA 2	10
比較例 1		IPA 5	
比較例 2		AS 0.8	
比較例 3	MBAM 0.03	MAS 0.3	
比較例 4	DMAM 0.8	MAS 0.4	
比較例 5	DMAM 1	MAS 0.3	15

[0031] the inside of Table 1 and 2, and AM:acrylamide and a MAN:methacrylonitrile anionic monomer -- carrying out -- as AA:acrylic acid, IA:itaconic acid, FA:fumaric acid, NSS:sodium styrenesulfonate, and a cross linking agent -- as MBAM:methylenebis acrylamide, DMAM:dimethyl acrylamide, and a chain transfer agent -- IPA: -- DM:dimethylaminoethyl methacrylate and St:styrene are shown, respectively as isopropyl alcohol, MAS:meta-allyl compound sulfonic-acid soda, AS:allyl compound sulfonic-acid soda, and other monomers.

[0032] In one to example of comparison 5 example 1, the class or its operating rate of a copolymerization component was changed as shown in Table 1 and 2, and also the same actuation as an example 1 was performed, and various copolymer water solutions were obtained. In the examples 3-5 of a comparison, although product viscosity tended to obtain the thing 5000cps or more, since it lifting-came to be easy of rapid thickening and gelation in the second half of a polymerization reaction, viscosity control was performed in the chain transfer agent, the amount of catalysts, etc., and the product of hypoviscosity was obtained. the description of the obtained various copolymer water solutions -- Table 3 is shown for a value.

[0033]

[Table 3]

	固形分 (%)	pH	粘度 (cps)	Mw (万)
実施例 1	20.4	4.7	8400	165
実施例 2	20.6	4.9	7200	143
実施例 3	20.7	5.2	6100	135
実施例 4	20.3	5.1	5200	172
実施例 5	20.4	4.9	6300	197
実施例 6	20.1	5.2	4800	138
実施例 7	20.2	5.3	4400	126
実施例 8	20.4	5.1	5100	221
実施例 9	20.5	5.3	3700	126
実施例 10	20.1	5.2	5600	173
実施例 11	20.3	5.2	4900	152
比較例 1	20.4	4.8	9700	48
比較例 2	20.6	4.9	7600	43
比較例 3	20.7	5.1	2800	145
比較例 4	20.5	5.0	3900	161
比較例 5	20.3	5.3	1800	168

[0034]

[The coating approach] The basis weight of 43g/m<sup>2</sup> Newspaper stencil paper was cut out to 12cm long and 24cm wide, and the upper part of paper was fixed with the Scotch tape on the flat glass plate. The compound polymer was diluted with water to 3% and 2%, and coating was carried out to one side using the coating roll bar of No.3. the place which measured the liquid adsorption of coating liquid -- 8.2 g/m<sup>2</sup> it is -- 3% diluent -- 0.25 g/m<sup>2</sup> and 2% diluent -- 0.16 g/m<sup>2</sup> It was the amount of coating. It dried for 90 seconds with the drum dryer immediately adjusted to 105 degrees C after coating, and sample paper was obtained. Evaluation was carried out for the obtained sample paper after gas conditioning one whole day and night by the air conditioned room (temperature of 20 degrees C, 65% of humidity).

[0035]

[The evaluation approach] Measurement was performed according to the approach shown below.

- RI pick : the display which observed a RI-II mold printing testing machine (product made from \*\*\*\*\*), Toyo Ink, the ink tuck 15, the amount of ink of 2ml, rotational frequency 60rpm, and the \*\*\*\*\* condition after printing with the naked eye, made 5 good, and made 1 \*\* estimated. The numeric value was expressed as the average of printing evaluation of five sheets.

- Internal reinforcement : internal bond tester (Kumagaya Riki Kogyo K.K. make)

- Breaking length : JIS P 8113 [0036]

[Table 4]

	R I ピック		インターナル・ボンド		裂断長	
	(a)	(b)	(a)	(b)	(a)	(b)
実施例 1	3.7	4.6	1.41	1.50	2.80	2.90
実施例 2	4.0	4.5	1.40	1.48	2.79	2.88
実施例 3	3.9	4.6	1.39	1.48	2.82	2.93
実施例 4	4.1	4.7	1.42	1.52	2.83	2.96
実施例 5	4.3	4.8	1.44	1.56	2.81	2.93
実施例 6	4.2	4.9	1.45	1.54	2.80	2.94
実施例 7	4.1	4.8	1.43	1.53	2.82	2.93
実施例 8	4.2	4.6	1.41	1.50	2.79	2.91
実施例 9	3.9	4.4	1.40	1.51	2.76	2.87
実施例 10	4.0	4.5	1.42	1.53	2.81	2.89
実施例 11	4.1	4.6	1.44	1.54	2.78	2.86
比較例 1	3.1	4.0	1.37	1.44	2.72	2.84
比較例 2	3.3	4.1	1.36	1.45	2.71	20.82
比較例 3	3.5	4.2	1.34	1.42	2.73	2.80
比較例 4	3.4	4.2	1.35	1.43	2.74	2.83
比較例 5	3.6	4.3	1.36	1.46	2.76	2.84

(a) : 塗工量 - 0.16 g/m<sup>2</sup>

(b) : 塗工量 - 0.25 g/m<sup>2</sup>

[Translation done.]